Supporting Information

Impact of Peripheral Alkyl Chain Length on Mesocrystal Assemblies of G2 Dendrons

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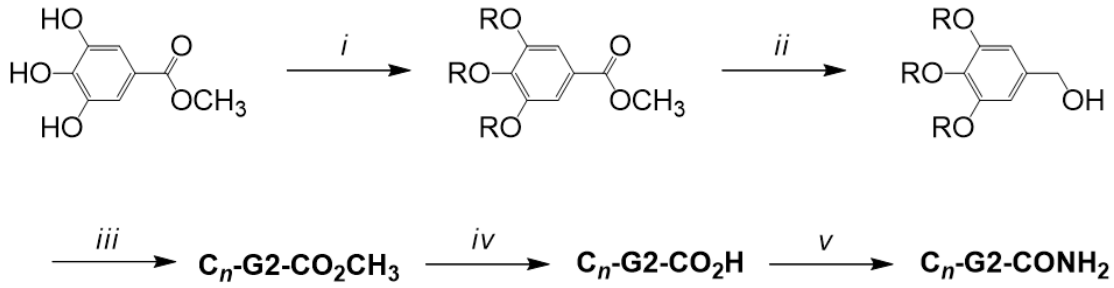
Synthesis procedure



All reagents were purchased from Sigma-Aldrich, TCI, Alfa Aesar, Duksan, or Fluka. The commercial products of dichloromethane (CH_2Cl_2), n-hexane, tetrahydrofuran (THF), and methanol (CH_3OH) were freshly distilled before each use, and all other chemicals were used as received without further purification. A series of C_n dendrons were synthesized by a convergent method reported in a previous study using different 1-bromoalkanes with carbon numbers of n = 18, 14, 12, 10, and 8.[1] Reagents and Conditions: (i) 1-bromododecane, K_2CO_3, 18-Crown-6, THF, reflux, 72 hr; (ii) $LiAlH_4$, THF, 0 °C, 3 h; (iii) methyl 3,5-dihydroxybenzoate, PPh_3, DIAD, THF, 0 °C, sonic 1 h; (iv) PPh_3, phthalimide, DIAD, THF, 0 °C, sonic 1 h; then $H_2NNH_2 \cdot H_2O$, THF/MeOH (5/1), reflux, 1 h. (v) 6 M NaOH, THF, reflux, 24 h.

Reference

1. T. Jun, H. Park, S. Jeon, S. Jo, H. Ahn, W.-D. Jang, B. Lee and D. Y. Ryu, *Journal of the American Chemical Society*, 2021, **143**, 17548-17556.

Supporting Figures

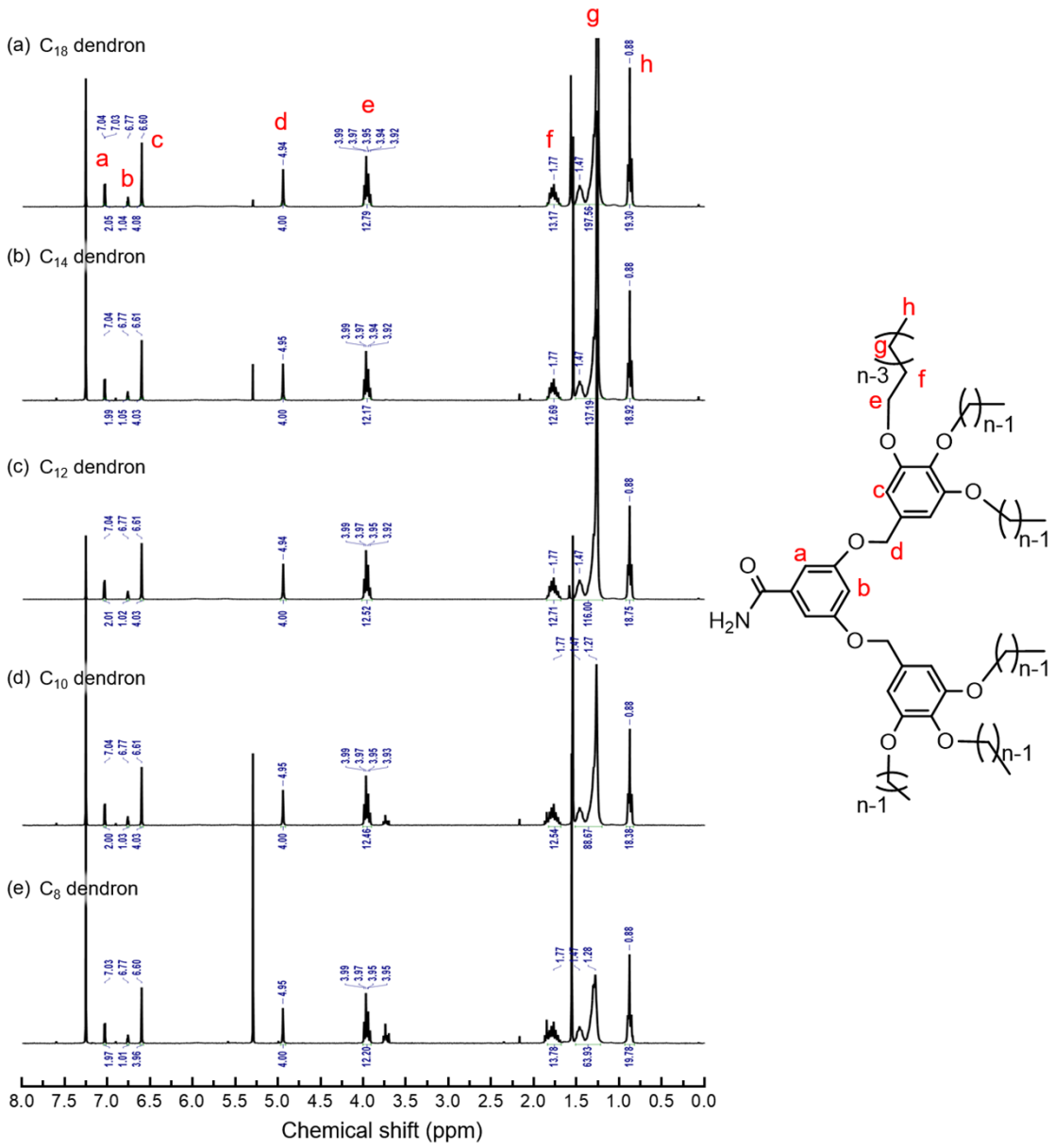


Fig. S1 ^{1}H NMR spectra of (a) C_{18}, (b) C_{14}, (c) C_{12}, (d) $C_{10,}$ and (e) C_{8} dendrons in $CDCl_3$ solvent.

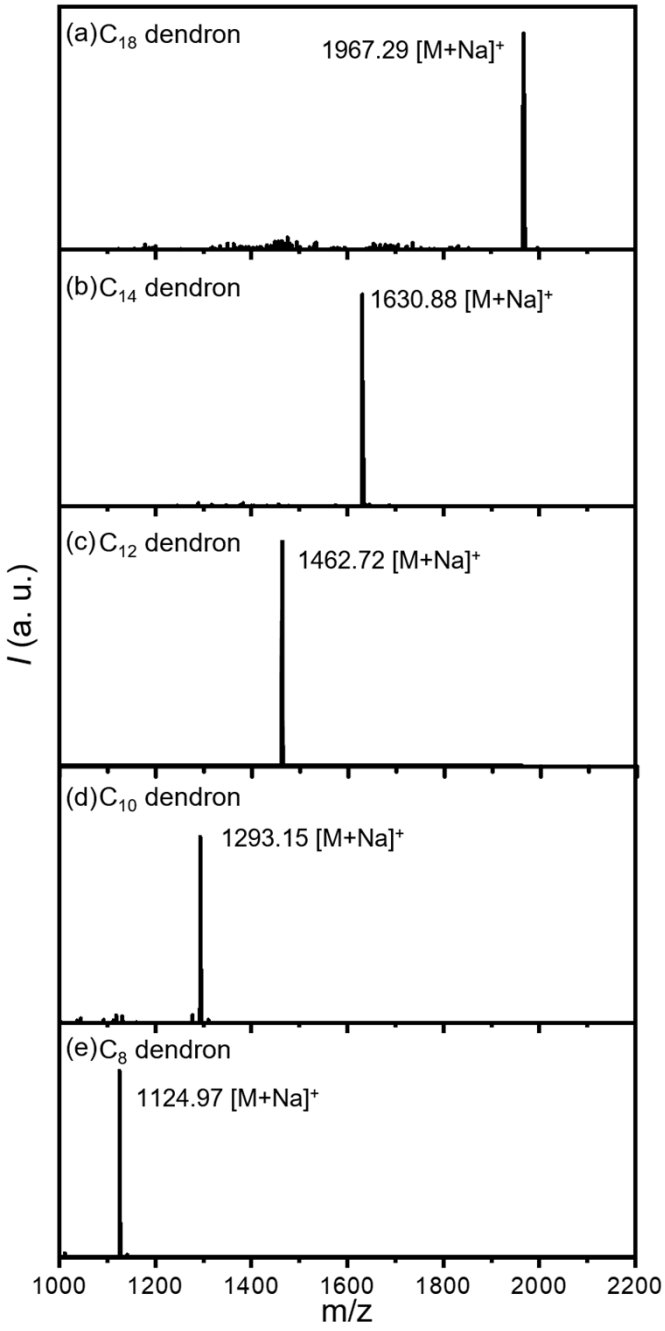


Fig. S2 MALDI-TOF mass spectra of (a) C_{18}, (b) C_{14}, (c) C_{12}, (d) C_{10}, and (e) C_8 dendrons.

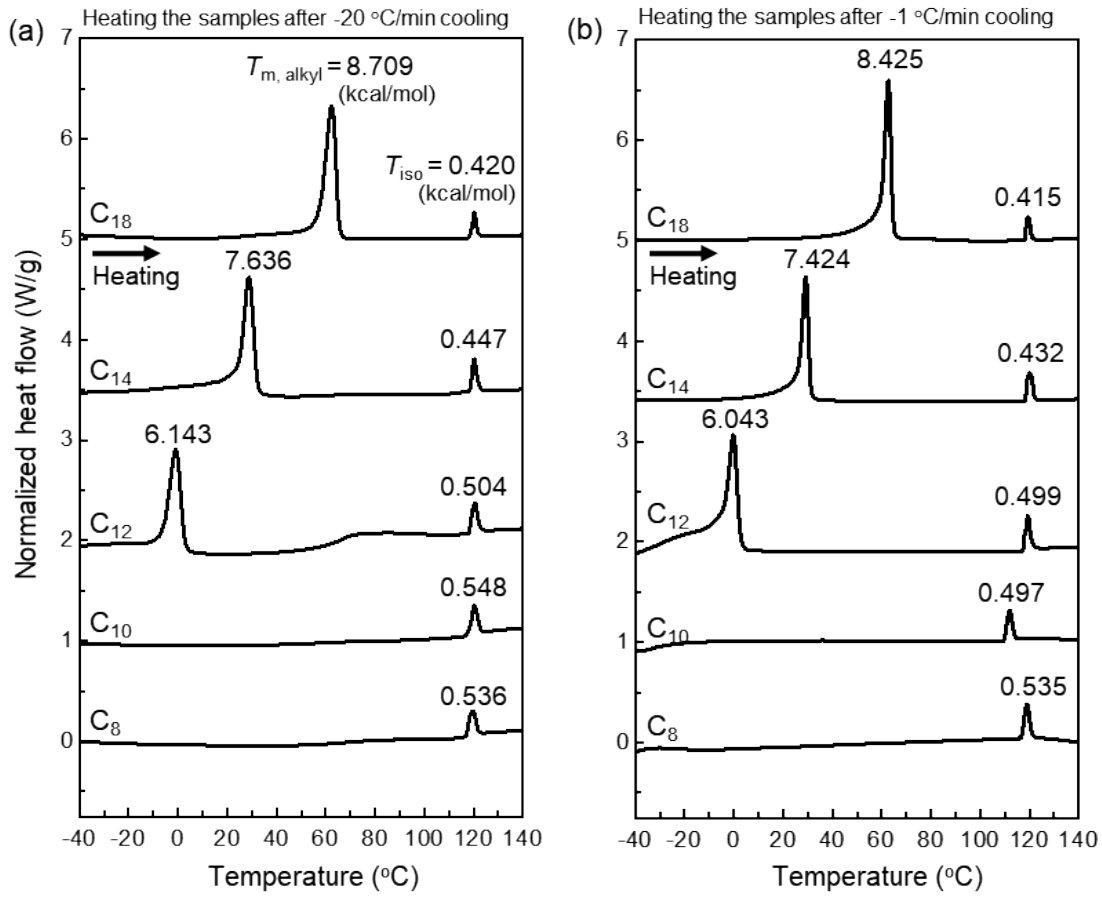


Fig. S3 DSC thermograms of the C_n dendrons prepared by (a) -20 and (b) -1 °C/min cooling processes, measured at the heating rate of 20 °C/min from -40 to 140 °C. The numbers on the peaks denote the magnitude of enthalpic change ($|\Delta H|$) at transitions as a unit of kcal/mol.

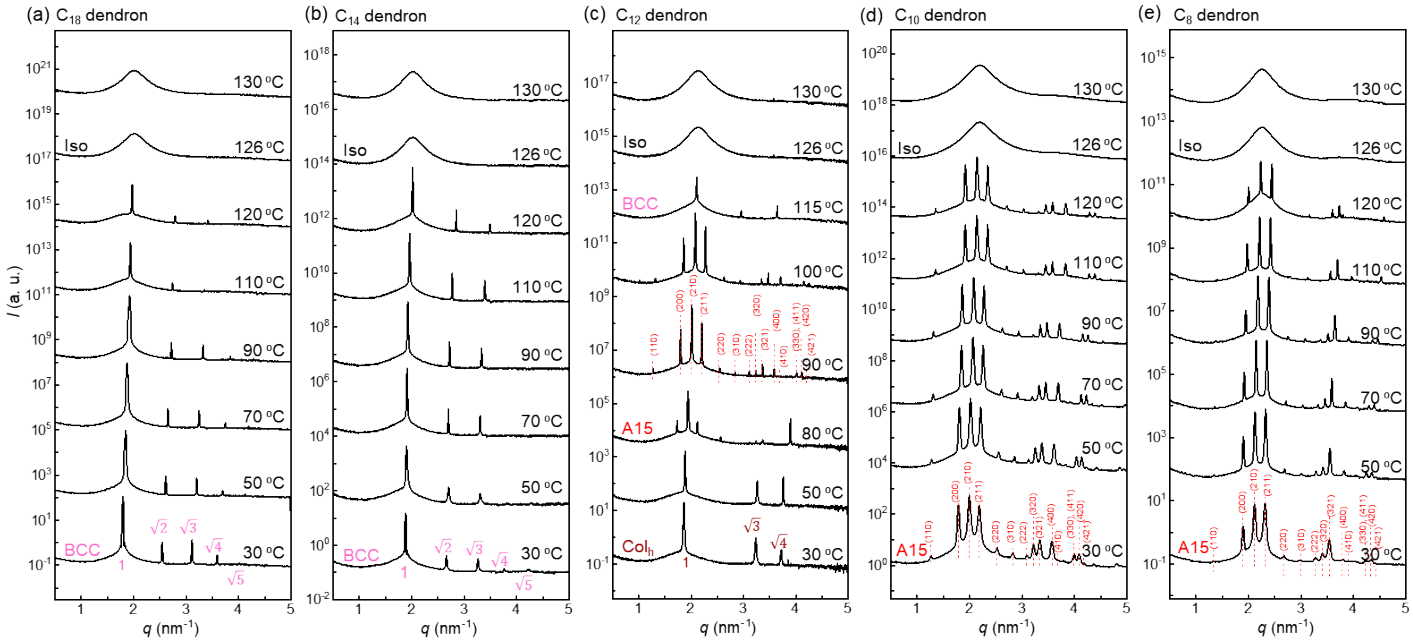


Fig. S4 SAXS intensity profiles for as-cast (a) C_{18}, (b) C_{14}, (c) C_{12}, (d) C_{10}, and (e) C_8 dendrons recorded at target temperatures during the stepwise heating process with a constant interval of 5 min considering the relatively rapid kinetics of dendrons in forming the mesocrystal structures.

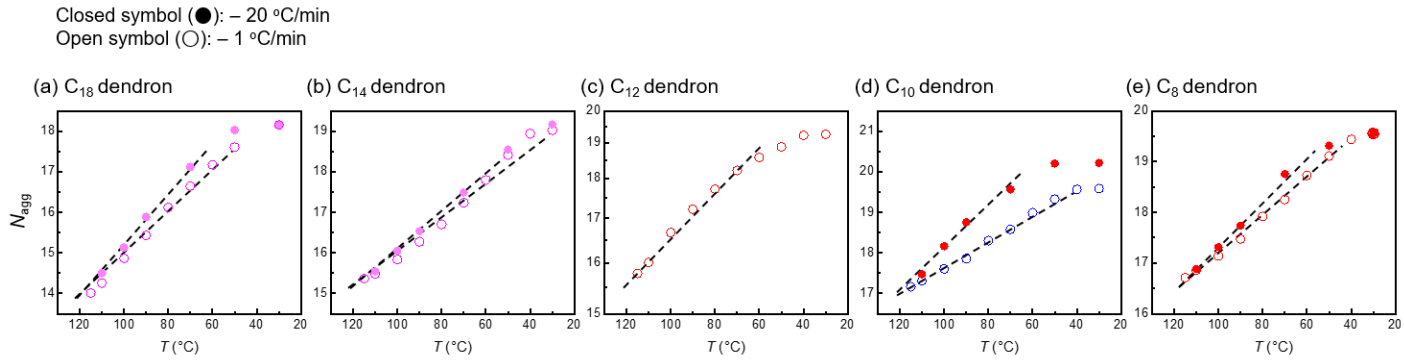


Fig. S5 N_{agg}s of (a) C_{18}, (b) C_{14}, (c) C_{12}, (d) C_{10}, and (e) C_8 dendrons during the fast- and slow-cooling processes. The closed and open symbols denote N_{agg}s from the fast- and slow-cooling processes, respectively, and the dotted lines guide initial rates of $|dN_{agg}/dT|$ for the C_n dendrons.

Supporting Table

Table S1. Structural analysis of representative supramolecular dendron assemblies

Sample	C_{18} dendron	C_{14} dendron	C_{12} dendron	C_{10} dendron	C_8 dendron
M_w **(g/mol)**	1944	1607	1439	1271	1102
ρ **(g/cm^3)**	0.970	0.973	0.975	0.978	0.981
Phase at fast cooling	BCC	BCC	Col_h [d]	A15	A15
$\bar{R}$ **(nm) at 110 & 30 °C** [a]	2.273 / 2.440	2.172 / 2.325	-	2.074 / 2.184	1.962 / 2.064
N_{agg} **at 110 & 30 °C** [b]	14.64 / 18.23	15.55 / 19.11	-	16.52 / 20.09	16.86 / 19.67
a **(=** b**),** c **(nm) at 110/30 °C**	4.616, 4.616 / 4.956, 4.956	4.411, 4.411 / 4.722, 4.722	-	6.687, 6.687 / 7.041, 7.041	6.325, 6.325 / 6.654, 6.654
$\Delta V/V$ [c]	0	0	-	0.0119	0.0119
Phase at slow cooling	BCC	BCC	BCC / A15	σ	A15
$\bar{R}$ **(nm) at 110 & 30 °C**	2.269 / 2.437	2.170 / 2.320	2.258 / 2.093	2.071 / 2.151	1.961 / 2.060
N_{agg} **at 110 & 30 °C**	14.73 / 18.15	15.59 / 19.00	16.09 / 19.46	16.47 / 19.50	16.88 / 19.55
a **(=** b**),** c **(nm) at 110 & 30 °C**	4.608, 4.608 / 4.950, 4.950	4.407, 4.407 / 4.712, 4.712	4.586, 4.586 / 6.748, 6.748	12.380, 7.283 / 12.859, 7.564	6.322, 6.322 / 6.641, 6.641
$\Delta V/V$	0	0	0 / 0.0118	0.0412	0.0119

[a]Mean particle radius ($\bar{R}$) was calculated by $V = 4\pi R^3/3 = n^{-1}\sum_{i=1}^{n} V_i$, where V_i is the i^{th} volume of n particles.

[b]$Nagg = \bar{R}^3 N_A \rho/(3M_w)$, where N_A, ρ, and M_w denote Avogadro's number (6.022×10^{23}/mol), the density measured at 30 °C, and the molecular weight of each dendron, respectively.

[c]Particle size diversity $\Delta V/V = n^{-1}\sum_{i=1}^{n} |V_i - V|/V.$

[d]Since the Col_h structure is not a sphere-packing phase.